A second program introduces the sphere radius $x_s$, and using the quantities $(A_{L'}{}^{L}-\delta_{L'0}U_{\mathrm{av}})$ calculates the Ewald coefficients, which are tabulated in Tables I–III. For $U_{\mathrm{av}}$ and $U_{\mathrm{sq}}{}^{L}$, $\epsilon=8$ was used, again so that the results are independent of $\epsilon$. To insure convergence, these sums were carried over 1800 stars, or about 73 000 vectors, up to a magnitude of $32.7(2\pi/a)$. The coefficients are all accurate to the number of decimal places given in the tables.

The coefficients $U_{\mathrm{q}}{}^{L}$ are a slightly different case, since they depend heavily on $\epsilon$. The particular $\epsilon$'s chosen, $\epsilon=3.50$, 3.68, and 3.48 for $L=0$, 4, and 6, were picked so that reasonable convergence is achieved in the first 29 stars, so that the series may be truncated after the vector $(4,4,4)(2\pi/a)$. Further, with an application to lithium in mind,[7] the $L=4$ and $L=6$ series need not converge as much as the dominant $L=0$ series, owing to the small multipole moments for higher $L$ in lithium. In short, the $\epsilon$'s can be chosen for each $L$ to suit a given application. For lithium, the coefficients in Table III give the potential to an accuracy of about three significant figures, or within 0.00005 Ry in the plane-wave region.

*Note added in proof:* The author has recently become aware of a very similar approach to this potential problem. See B. R. A. Nijboer and F. W. DeWette, Physica **23**, 309 (1957); **24**, 1105 (1958).

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# Self-Consistent Augmented-Plane-Wave Method*

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The augmented-plane-wave method for energy-band calculations is presented in a form which handles a general one-electron crystalline potential, rather than the restricted "muffin-tin" potential which has traditionally been used. From the wave functions resulting from the band calculation, the total crystalline charge density is found, and from this, a new potential is found, making an iterative self-consistent calculation possible. As an example, the method has been applied to body-centered cubic (bcc) lithium. The results of two energy-band calculations are reported. One used the average free-electron-exchange approximation suggested by Slater. The second used two-thirds of this exchange.

## I. INTRODUCTION

THE augmented-plane-wave (APW) method, originally proposed by Slater,[1–3] solves the energy-band problem by dividing a crystal into several parts. A sphere is constructed about each atomic site. The wave function is then expanded inside each APW sphere in terms of radial functions multiplied by spherical harmonics; in the region between the spheres, the plane-wave region, the wave function is expanded in a Fourier series of plane waves. Wood[4] has discussed the method for a monatomic crystal, using group-theoretical methods to reduce the size of the secular equation. Ern and Switendick[5] have generalized the method to any number of atoms per unit cell. Traditionally, the model for the one-electron potential energy has been limited to a muffin-tin form, in which the potential is assumed to be spherically symmetric within each APW sphere, and constant in the plane-wave region. The method is not limited to this model. Marcus[6] has considered the non-muffin-tin contributions to the matrix elements which enter into the eigenvalue problem, and DeCicco[7] included a nonconstant potential in the plane wave region in his calculation of energy bands in KCl. The first aim of the present paper is to present the more general APW method for any crystal with a symmorphic space group, allowing the use of an arbitrary potential, limited only by the assumption that it have the full symmetry of the crystal, and using the symmetry of the crystal to reduce the size of the secular determinant and to simplify the matrix elements as much as possible for use in numerical calculations. Section II presents a set of basis functions useful in this connection.

Section IV gives an expression for the electron density found in the energy-band calculation, and also considers the normalization of the one-electron wave functions. From this, the Coulomb potential energy is found. The average free-electron-exchange approximation is

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also discussed briefly. The formalism presented allows an iterative calculation to achieve self-consistency. Several self-consistent APW calculations have been made in the past,[7–14] but these have been limited to a muffin-tin model for the potential and also for the charge density.

Finally, two self-consistent energy-band calculations for bcc lithium are reported. One used the average free-electron-exchange approximation as proposed by Slater.[15] The second uses two-thirds of Slater's exchange, as proposed by Gaspar[16] and by Kohn and Sham.[17]

## II. CRYSTALLINE SYMMETRY AND LATTICE HARMONICS

The crystal is assumed, in this paper, to have a symmorphic space group. The Bravais lattice associated with the crystal is defined by a set of lattice vectors $\mathbf{R}$. Let there be $n$ atoms per unit cell. Then, with respect to the points in the Bravais lattice, the nuclei within a unit cell are located at the positions $\mathbf{r}_i$, $i=1, \cdots, n$.

The crystal is left invariant under a translation through a distance $\mathbf{R}$. There is also a point group of order $G$, consisting of rotations $S$ which take the crystal into itself. For a symmorphic space group it can be shown that it is possible to consider the translational group and the point group separately, without dealing with the full space group explicitly. Associated with the Bravais lattice there is a reciprocal lattice, defined by a set of vectors $\mathbf{K}$. These vectors have the property that $\mathbf{K}\cdot\mathbf{R}$ is equal to an integer multiplied by $2\pi$.

In the APW method a sphere of radius $R_{si}$ is constructed about the $i$th atom. The radius is arbitrary, although it is assumed that no two spheres intersect, since in that case the definition of functions within the volumes of intersection is ambiguous. It is customary, but not necessary, to choose the spheres to be tangent to their nearest neighbors. Within each APW sphere, all functions of interest are expanded in terms of radial functions multiplied by angular functions about the center of the sphere. In the plane-wave region, outside all of the spheres, the functions are expanded in Fourier series. Of special interest here are functions, for example the potential $V(\mathbf{r})$ or the charge density $\rho(\mathbf{r})$, which have the full symmetry of the crystal. Let $f(\mathbf{r})$ be such a function. The function may then be written

$$f(\mathbf{r})=\begin{bmatrix} \sum\limits_{L\nu} f_{L\nu i}(|\mathbf{r}-\mathbf{r}_i|)W_{L\nu i}(\mathbf{r}-\mathbf{r}_i), & \text{when } |\mathbf{r}-\mathbf{r}_i|\leq R_{si} \\ \sum\limits_{\mathbf{K}} f(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}}, & \text{when } |\mathbf{r}-\mathbf{r}_i|>R_{si} \text{ for all } i \end{bmatrix}.$$

Here and elsewhere throughout the paper, the first line gives the form of the function within the $i$th sphere, translated, if necessary, back into the zeroth unit cell, so that $|\mathbf{r}-\mathbf{r}_i|\leq R_{si}$. The second line gives the form of the function in the plane-wave region, where $|\mathbf{r}-\mathbf{r}_i|>R_{si}$ for all $i$.

Within the $i$th sphere, it is possible to expand any function in terms of spherical harmonics, but for a function with the symmetry of the crystal lattice, it is more efficient to expand in terms of the lattice harmonics[18] $W_{L\nu i}(\mathbf{r})$. These are surface harmonics, a complete orthonormal set of the linear combinations of spherical harmonics which have the symmetry of the crystal lattice. They may be chosen to be real. The following properties can be shown to be consistent; they do not uniquely determine the harmonics $W_{L\nu i}(\mathbf{r})$, but are sufficient for the present purpose:

$$W_{L\nu i}(\mathbf{r})=W_{L\nu i}{}^*(\mathbf{r})=\sum_m C_{Lm\nu i}Y_{Lm}(\mathbf{r}),$$

$$\int_{4\pi} W_{L'\nu' i}(\mathbf{r})W_{L\nu i}(\mathbf{r})d\Omega=4\pi\delta_{L'L}\delta_{\nu'\nu}.$$

To find the coefficients $C_{Lm\nu i}$, it is sufficient to require that $RW_{L\nu i}(\mathbf{r})=W_{L\nu i}(R^{-1}\mathbf{r})=W_{L\nu i}(\mathbf{r})$ for any rotation $R$ from the point group $\{S\}$ such that $R\mathbf{r}_i=\mathbf{r}_i+\mathbf{R}$ is valid for some lattice vector $\mathbf{R}$. If $T$ is a rotation from $\{S\}$ such that $T\mathbf{r}_i=\mathbf{r}_j+\mathbf{R}$ is valid, then the $i$th and $j$th atoms are considered to be equivalent, and it is convenient to choose the $C_{Lm\nu i}$ so that $TW_{L\nu i}(\mathbf{r})=W_{L\nu i}(T^{-1}\mathbf{r})=W_{L\nu j}(\mathbf{r})$. The reality of the lattice harmonics requires that $C_{L-m\nu i}=(-1)^m C_{Lm\nu i}$. The index $\nu$ accounts for the fact that there may be more than one lattice harmonic for each $L$. For $L=0$, $\nu$ can take on just one value, which is taken to be zero. In general, $\nu$ may take on from 0 to $2L+1$ values for each $L$.

In the plane-wave region, only reciprocal vectors $\mathbf{K}$ appear in the Fourier series. The series could be expressed in terms of symmetrized plane waves, but this does not seem to be advantageous.

## III. APW METHOD

The APW method finds the best solution to the one-electron Schrödinger's equation (in atomic units)

$$[-\nabla^2+V(\mathbf{r})]\psi(\mathbf{r})=\epsilon\psi(\mathbf{r})$$

by using the variational method and the augmented-plane-wave basis functions given below. The potential

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is assumed to have the full symmetry of the crystal, and to be known in the form

$$V(\mathbf{r})=\begin{cases} V_{mi}(|\mathbf{r}-\mathbf{r}_i|)+\sum_{L\nu} V_{L\nu i}(|\mathbf{r}-\mathbf{r}_i|)W_{L\nu i}(\mathbf{r}-\mathbf{r}_i) \\ V_{m0}+\frac{1}{\Omega}\sum_{\mathbf{K}} V(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}} \end{cases}. \quad (1)$$

Note that $V(\mathbf{K})$ is equal to a Fourier coefficient multiplied by the volume of a unit cell.

The first term in each line, with the subscript $m$, is the muffin-tin part of the potential. The remaining terms represent deviations from this form. Note that the $L=0$ term in the first line also has a muffin-tin contribution. Ordinarily this term would be chosen to be zero, but this is not necessary. The Fourier series in the second line is not uniquely determined by Eq. (1). It turns out that the matrix elements appearing in the secular equation are considerably simpler if the series is chosen so that it is identically zero inside each APW sphere:

$$\sum_{\mathbf{K}} V(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}}=0 \quad \text{for } |\mathbf{r}-\mathbf{r}_i|<R_{si} \text{ for all } i.$$

With this additional requirement, the coefficients $V(\mathbf{K})$ are uniquely determined. The Fourier series could give a constant contribution in the plane-wave region, but this would ordinarily be absorbed by the muffin-tin term $V_{m0}$, which traditionally has been set equal to zero by shifting the zero of energy. It is noted that if the $i$th and $j$th atoms are equivalent, then $V_{mj}(r)=V_{mi}(r)$ and $V_{L\nu j}(r)=V_{L\nu i}(r)$. Also, $V(S\mathbf{K})=V(\mathbf{K})$, so that two Fourier coefficients are equal if they correspond to reciprocal lattice vectors in the same star.

The unsymmetrized basis functions, or raw APW's, depend only on the muffin-tin part of the potential, namely, on $V_{mi}(r)$. Let $u_{li}(r,\epsilon_t)$ be a solution, regular at the origin, of the radial Schrödinger equation

$$[-r^{-2}(d/dr)r^2(d/dr)+l(l+1)r^{-2}+V_{mi}(r)] \times u_{li}(r,\epsilon_t)=\epsilon_t u_{li}(r,\epsilon_t).$$

The solution is normalized so that $u_{li}(R_{si},\epsilon_t)=1$. The raw APW's are

$$\phi_{\mathbf{k}_g}(\mathbf{r})=\begin{cases} \Omega^{-1/2}e^{i\mathbf{k}_g\cdot\mathbf{r}_i}\sum_{lm} 4\pi i^l j_l(k_gR_{si})u_{li}(|\mathbf{r}-\mathbf{r}_i|,\epsilon_t) \\ \qquad\times Y_{lm}^*(\mathbf{k}_g)Y_{lm}(\mathbf{r}-\mathbf{r}_i) \\ \Omega^{-1/2}e^{i\mathbf{k}_g\cdot\mathbf{r}} \end{cases}.$$

The wave vector $\mathbf{k}_g=\mathbf{k}+\mathbf{K}_g$ determines the transformation properties of the state under question. $\mathbf{k}$ is the reduced wave vector, lying within the first Brillouin zone, and determines the translational properties of the basis function. $\mathbf{K}_g$ is the $g$th reciprocal lattice vector. $\Omega$ is the volume of the unit cell, and $j_l(x)$ is a spherical Bessel function. The basis function $\phi_{\mathbf{k}_g}(\mathbf{r})$, as a result of the definition, is continuous at all points on the surfaces of the APW spheres, but the first derivative is not continuous.

The size of the determinant in the secular equation is effectively reduced if basis functions are used which transform irreducibly under the operations of the group of the wave vector. A suitable set of symmetrized APW's, transforming as the $i$th partner in the $\alpha$th irreducible representation is

$$\Phi_{gj}^{\alpha i}(\mathbf{r})=\sum_R \Gamma_\alpha^*(R)_{ij}\phi_{R\mathbf{k}_g}(\mathbf{r}).$$

The sum over $R$ is the sum over all the operations in the group of the wave vector, namely, those rotations in $\{S\}$ such that $R\mathbf{k}_g=\mathbf{k}_g+\mathbf{K}$ for some $\mathbf{K}$ in the reciprocal lattice. The second projection operator index $j$ is needed in the case that more than one linearly independent function with the proper transformation properties can be projected from the same $\phi_{\mathbf{k}_g}(\mathbf{r})$. $\Gamma_\alpha(R)_{ij}$ is the element from the $i$th row and $j$th column of the matrix representative of the operation $R$ in the $\alpha$th irreducible representation. It is always possible to choose this representation to be unitary, and it is assumed that this has been done.

The APW wave functions are taken to be

$$\psi_{\mathbf{k}}^{\alpha i}(\mathbf{r})=\sum_{gj} A_{gj}\Phi_{gj}^{\alpha i}(\mathbf{r}),$$

where the components $A_{gj}$ of the eigenvector are to be determined by the variational method. This leads to the secular equation

$$\det|(H-\epsilon)_{gj,g'j'}|=0,$$

where $\epsilon$ is the eigenenergy. The APW matrix elements are

$$(H-\epsilon)_{gj,g'j'}=\frac{n_\alpha\Omega}{G_k}\int_\Omega \Phi_{gj}^{\alpha i*}(\mathbf{r})(H-\epsilon)\Phi_{g'j'}^{\alpha i}(\mathbf{r})d\mathbf{r},$$

where $n_\alpha$ is the dimensionality of the irreducible representation, and $G_k$ is the order of the group of the wave vector. The integration is over the volume $\Omega$ of any one unit cell. The constant factor $n_\alpha\Omega/G_k$ has been included to simplify the matrix elements. It is the same for every element in the determinant, and hence does not effect either the eigenenergy $\epsilon$ or the eigenvector $\{A_{gj}\}$. Using standard manipulations in group theory, the matrix elements can be reduced to

$$(H-\epsilon)_{gj,g'j'}=\Omega\sum_R \Gamma_\alpha^*(R)_{jj'}\int_\Omega \phi_{\mathbf{k}_g}^*(\mathbf{r})(H-\epsilon)\phi_{R\mathbf{k}_{g'}}(\mathbf{r})d\mathbf{r}.$$

It is noted that the matrix element does not depend on the partner index $i$. Finally, after a considerable amount of relatively straightforward analysis, it is found that the APW matrix element is

$$
\begin{aligned}
(H-\epsilon)_{gj,g'j'} &= \Omega(2\pi/a)^2\beta_{gj,g'j'} - \Omega(\epsilon - V_{m0})\alpha_{gj,g'j'} \\
&\quad + \sum_{il} {}^{00}\gamma_{gj,g'j'}{}^{lli}[R_{si}{}^2 u_{li}'(R_{si},\epsilon_t)] \\
&\quad + (\epsilon_t-\epsilon)\sum_{il} {}^{00}\gamma_{gj,g'j'}{}^{lli}\int_0^{R_{si}} r^2dr\,|u_{li}(r,\epsilon_t)|^2 \\
&\quad + \sum_{\mathbf{K}} \delta_{gj,g'j'}{}^{\mathbf{K}}V(\mathbf{k}) + \sum_{\substack{iL\nu ll' \\ l'\leq l}} {}^{L\nu}\gamma_{gj,g'j'}{}^{ll'i} \\
&\quad \times \int_0^{R_{si}} r^2dr\; V_{L\nu i}(r)u_{li}(r,\epsilon_t)u_{l'i}(r,\epsilon_t)\,.
\end{aligned}
$$

The symbols introduced in this expression are discussed in detail below.

$a$ is a scaling factor, to which all the lattice constants of the crystal are assumed to be proportional. The volume of the unit cell, $\Omega$, is then proportional to $a^3$. The dimensionless symmetry elements $\alpha$, $\beta$, $\gamma$, and $\delta$, as will be seen from their definitions below, do not depend on the potential, the energies $\epsilon_t$ and $\epsilon$, or the scaling factor $a$, but only on the crystal structure, the ratio $\Omega/a^3$, and the size of the APW spheres relative to $a$. The final results do not depend on $\Omega/a^3$, which is completely arbitrary, and may be chosen for convenience.

The logarithmic derivatives

$$u_{li}'(R_{si},\epsilon_t) = \frac{d}{dr}\ln[u_{li}(r,\epsilon_t)]_{r=R_{si}}\,,$$

on the other hand, depend on the spherically symmetric potentials $V_{mi}(r)$ and the trial energy $\epsilon_t$, but not on the symmetry of the crystal. Note that for the normalization used for $u_{li}(r,\epsilon_t)$, the ordinary and logarithmic derivatives, evaluated at the sphere radius, are equal.

It is practical and usual in implementing the APW method to set $\epsilon=\epsilon_t$, and to evaluate $\det|H-\epsilon_t|$ for a series of values of $\epsilon_t$. The eigenenergy $\epsilon$ is then found by inverse interpolation so that $\det|H-\epsilon|=0$. If this is done, then the term in the matrix elements involving the difference $\epsilon_t-\epsilon$ vanishes, and is correctly omitted from the calculation.

An alternative approach is to set the trial energy $\epsilon_t$ equal to some initial guess, and to solve for the eigenenergy $\epsilon$ in a conventional way, holding $\epsilon_t$ fixed. If $\epsilon$ is not then equal to $\epsilon_t$, the procedure is repeated, now using the $\epsilon$ just found as the new $\epsilon_t$. As Marcus[6] has pointed out, the convergence of this iterative procedure will depend significantly on the inclusion of the term involving the difference $\epsilon_t-\epsilon$ in the matrix elements, although in the limit of self-consistency ($\epsilon=\epsilon_t$), this term will make no contribution.

The symmetry elements are

$$\alpha_{gj,g'j'} = \sum_R \Gamma_\alpha{}^*(R)_{jj'}\Delta(\mathbf{k}_g - R\mathbf{k}_{g'})\,,$$

$$\beta_{gj,g'j'} = (a/2\pi)^2\sum_R \Gamma_\alpha{}^*(R)_{jj'}(\mathbf{k}_g\cdot R\mathbf{k}_{g'})\Delta(\mathbf{k}_g - R\mathbf{k}_{g'})\,,$$

$$
\begin{aligned}
&{}^{L\nu}\gamma_{gj,g'j'}{}^{ll'i} \\
&\quad = \sum_{Mn} d_{L\nu Mi}{}^n \sum_m G_{LM}(l,l',m) \\
&\quad\quad \times \sum_{\substack{\text{scos} \\ \nu p}} [{}^0X^{i*}{}_{\text{scos}}(l,m,\nu,g)_{pj}\; {}^nX^i{}_{\text{scos}}(l',\, M+m,\, \nu,\, g')_{pj'} \\
&\quad\quad + (-1)^{L+n}\; {}^0X^{i*}{}_{\text{scos}}(l',\, M+m,\, \nu,\, g)_{pj} \\
&\quad\quad\quad \times {}^nX^i{}_{\text{scos}}(l,m,\nu,g')_{pj'}]\,,
\end{aligned}
$$

$$\delta_{gj,g'j'}{}^{\mathbf{K}} = \sum_R \Gamma_\alpha{}^*(R)_{jj'}\delta(\mathbf{K}*(\mathbf{k}_g - R\mathbf{k}_{g'}))/n_K\,.$$

$\beta_{gj,g'j'}$ does not depend on $a$, since both $\mathbf{k}_g$ and $\mathbf{k}_{g'}$ are proportional to $1/a$. The new quantities will be discussed in the order they appear.

$$
\begin{aligned}
\Delta(\mathbf{K}) &= \Omega^{-1}\int_{PW} e^{-i\mathbf{K}\cdot\mathbf{r}}d\mathbf{r} \\
&= \delta_{\mathbf{K},0} - \sum_i 4\pi R_{si}{}^2\Omega^{-1}e^{-i\mathbf{K}\cdot\mathbf{r}_i}K^{-1}j_1(KR_{si})\,.
\end{aligned}
$$

The integration is over the plane-wave region of any one unit cell, and $\delta_{\mathbf{K},0}$ is a Kronecker $\delta$ function. Note that $\mathbf{k}_g - R\mathbf{k}_{g'}$ is always equal to some reciprocal lattice vector.

The symmetry elements ${}^{L\nu}\gamma_{gj,g'j'}{}^{ll'i}$ are associated, through $L$ and $\nu$, with the lattice harmonics. It is more convenient to calculate the symmetry elements associated with the spherical harmonics, and then to relate the needed elements to these through the real coefficients $d_{L\nu Mi}{}^n$, which are defined by requiring that the expression

$$
\begin{aligned}
F_{L\nu i}(r) &= \sum_m d_{L\nu mi}{}^0[(f_{Lmi}(r) + (-1)^m f_{L-mi}(r))] \\
&\quad + \sum_m d_{L\nu mi}{}^1[(f_{Lmi}(r) - (-1)^m f_{L-mi}(r))/i] \qquad (2)
\end{aligned}
$$

be valid for any function $f(\mathbf{r})$ with full crystalline symmetry, where

$$f(\mathbf{r}) = \sum_{L\nu} F_{L\nu i}(r)W_{L\nu i}(\mathbf{r}) = \sum_{lm} f_{lmi}(r)Y_{lm}(\mathbf{r})\,.$$

The coefficients are not uniquely defined, in general, but any set satisfying (2) will do.

The coefficients $G_{LM}(l,l',m)$ are proportional to Gaunt coefficients, that is, the integral over all angles of the product of three spherical harmonics:

$$G_{LM}(l,l',m)$$

$$=\frac{4\pi(4\pi)^{1/2}}{G}i^{l'-l}(-1)^{\frac{1}{2}(|m|+|M+m|-M)}(2-\delta_{l'l})(2l+1)$$

$$\times(2l'+1)\left[(2L+1)\frac{(l-|m|)!(l'-|M+m|)!}{(l+|m|)!(l'+|M+m|)!}\right]^{1/2}$$

$$\times\begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l & l' & L \\ -m & M+m & -M \end{pmatrix}.$$

Because of the properties of the 3-$j$ symbols[19]

$$\begin{pmatrix} l & l' & L \\ -m & M+m & -m \end{pmatrix},$$

$G_{LM}(l,l',m)$ is zero unless a triangle can be constructed with sides $l$, $l'$, and $L$; $l+l'+L$ is an even number; and the following inequalities hold: $-L\leq M\leq L$; $-l\leq m\leq l$; and $-l'\leq M+m\leq l'$. These establish the range of $M$ and $m$ in the summations.

The quantities $X$ are defined by

$${}^{n}X^{i}{}_{\mathrm{scos}}(l,m,\nu,g)_{pj}=\sum_{R}\Gamma_\alpha{}^*(R)_{pj}e^{iT_\nu R\mathbf{k}_g\cdot\mathbf{r}_i}j_l(k_gR_{si})$$

$$\times P_{l|m|}(\cos\vartheta_{T_\nu R\mathbf{k}_g})\,\mathrm{scos}^{(n)}(m\varphi_{T_\nu R\mathbf{k}_g}).$$

The symbol scos stands for the two functions, sine and cosine, and the sum over scos means a sum over the two functional forms. The superscript $n$ on $\mathrm{scos}^{(n)}\varphi$ can be considered to be a derivative with respect to the argument. By definition, if scos=sin, then $\mathrm{scos}^{(0)}\varphi=\sin\varphi$ and $\mathrm{scos}^{(1)}\varphi=\cos\varphi$; if scos=cos, then $\mathrm{scos}^{(0)}\varphi=\cos\varphi$ and $\mathrm{scos}^{(1)}\varphi=-\sin\varphi$. The function $P_{lm}(\cos\vartheta)$ is an associated Legendre polymonial. The sum over $\nu$ is a sum over the left cosets of the group $\{R\}$ of the wave vector $\mathbf{k}$. The rotation $T_\nu$ is any one of the operations in the $\nu$th left coset. The choice of which member of the coset is to be $T_\nu$ is arbitrary, but once made, is considered to be fixed. $\vartheta_{T_\nu R\mathbf{k}_g}$ and $\varphi_{T_\nu R\mathbf{k}_g}$ are the angular coordinates of the vector $T_\nu R\mathbf{k}_g$.

In the interest of comparison with previous APW calculations, as well as for numerical simplification, it is worth noting that

$${}^{0\nu}\gamma_{gj,g'j'}{}^{ll'i}=\delta_{\nu0}\delta_{l'l}\,{}^{00}\gamma_{gj,g'j'}{}^{lli}$$

and

$${}^{00}\gamma_{gj,g'j'}{}^{lli}=4\pi(2l+1)j_l(k_gR_{si})j_l(k_{g'}R_{si})\sum_{R}\Gamma_\alpha{}^*(R)_{jj'}$$

$$\times P_l\left(\frac{\mathbf{k}_g\cdot R\mathbf{k}_{g'}}{k_gk_{g'}}\right)\times\frac{1}{G}\sum_{S}e^{-i(\mathbf{k}_g-R\mathbf{k}_{g'})\cdot S\mathbf{r}_i}.$$

Note also that ${}^{L\nu}\gamma_{gj,g'j'}{}^{ll'i}={}^{L\nu}\gamma_{gj,g'j'}{}^{ll'i'}$ is valid if the $i$th and $i'$th atoms are equivalent.

Finally, $\delta(\mathbf{K}*\mathbf{K}')$ is a $\delta$ function which is defined to be 1 if $\mathbf{K}$ and $\mathbf{K}'$ lie in the same star, so that $S\mathbf{K}=\mathbf{K}'$ for some rotation $S$. If $\mathbf{K}$ and $\mathbf{K}'$ are in different stars, then the $\delta$ function is equal to 0. $n_K$ is the number of vectors in the star of $\mathbf{K}$. From this definition, it follows that the contribution to the matrix element from the Fourier potential may also be written as

$$\sum_{\mathbf{K}}\delta_{gj,g'j'}{}^{\mathbf{K}}V(\mathbf{K})=\sum_{R}\Gamma_\alpha{}^*(R)_{jj'}V(\mathbf{k}_g-R\mathbf{k}_{g'}).$$

## IV. ELECTRON DENSITY AND NORMALIZATION

The electron density from a given state does not in general have the symmetry of the crystal. It can be shown, however, that the collection of all the states which transform as partners in the $\alpha$th irreducible representation for the wave vector $\mathbf{k}$, along with all the partners for all the other states with wave vectors in the star of $\mathbf{k}$, are degenerate in energy. Further, since these $Gn_\alpha/G_k$ states will therefore fill with equal probability, it can be shown that the total electron density, due to the electrons in these states, will have the symmetry of the crystal. Finally, to get the total electron density, it will suffice to project the part with crystalline symmetry out of the density for any one state, and multiply by the number of states.

The number $Gn_\alpha/G_k$ of states should be multiplied by two in order to get the total for spin up and spin down.

In this sense, the electron density for one state is

$$\rho_\alpha(\mathbf{r})=\frac{1}{G}\sum_{S}\psi_{S\mathbf{k}}{}^{\alpha i*}\psi_{S\mathbf{k}}{}^{\alpha i}=\begin{bmatrix}\displaystyle\sum_{L\nu}\rho_{L\nu i}(|\mathbf{r}-\mathbf{r}_i|)W_{L\nu i}(\mathbf{r}-\mathbf{r}_i)\\ \displaystyle\sum_{\mathbf{K}}\rho(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}}\end{bmatrix}. \tag{3}$$

It is found that

$$\rho_{L\nu i}(r)=\sum_{ll',\,l'\leq l}u_{li}(r,\epsilon_t)u_{l'i}(r,\epsilon_t)\frac{G_k}{4\pi\Omega n_\alpha}$$

$$\times\sum_{gj,g'j'}A_{gj}{}^*A_{g'j'}\,{}^{L\nu}\gamma_{gj,g'j'}{}^{ll'i},$$

and

$$\rho(\mathbf{K})=\frac{G_k}{\Omega n_\alpha}\sum_{gj,g'j'}A_{gj}{}^*A_{g'j'}\delta_{gj,g'j'}{}^{\mathbf{K}}.$$

The components $A_{gj}$ of the eigenvector, found to within a normalization factor by the variational method, can be normalized so that the state represents one electron per unit cell:

$$\frac{G_k}{n_\alpha}\sum_{gj,g'j'}A_{gj}{}^*A_{g'j'}$$

$$\times\left[\alpha_{gj,g'j'}+\frac{1}{\Omega}\sum_{il}{}^{00}\gamma_{gj,g'j'}{}^{lli}\int_0^{R_{si}}r^2dr\,|u_{li}(r,\epsilon_t)|^2\right]=1.$$

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[19] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, *The 3-j and 6-j Symbols* (Technology Press, Massachusetts Institute of Technology, Cambridge, 1959).

The first term in square brackets corresponds to the fraction of an electron in the plane-wave region, while the second term is a sum over the fractions in each of the APW spheres.

## V. COULOMB POTENTIAL ENERGY

Once the electron density (3) is known for each occupied state, the total charge density is easily found. Taking into account also the nuclear charge, the crystalline charge density is in the form

$$P(\mathbf{r})=\left[\begin{array}{l} -\sum\limits_{L\nu}\rho_{L\nu i}(|\mathbf{r}-\mathbf{r}_i|)W_{L\nu i}(\mathbf{r}-\mathbf{r}_i)+\dfrac{Z_i\delta(|\mathbf{r}-\mathbf{r}_i|)}{4\pi|\mathbf{r}-\mathbf{r}_i|^2} \\ -\sum\limits_{\mathbf{K}}\rho(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}} \end{array}\right].$$

The negative sign is due to the fact the $\rho(\mathbf{r})$ is an electron density, while $P(\mathbf{r})$ is a charge density. $Z_i$ is the charge on the nucleus at the center of the $i$th sphere. In order to find the Coulomb potential energy, the charge density is conveniently decomposed into several parts, so that

$$P(\mathbf{r})=P_1(\mathbf{r})+\sum_{L\nu i}P_{2L\nu i}(\mathbf{r})+\sum_{L\nu i}P_{3L\nu i}(\mathbf{r}),$$

where

$$P_1(\mathbf{r})=-\sum_{\mathbf{K}\neq 0}\rho(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}}\quad\text{for all }\mathbf{r}.$$

$$P_{2L\nu i}(r)=\left[\begin{array}{l} \Big(-\rho_{L\nu i}(|\mathbf{r}-\mathbf{r}_i|)+i^L\sum\limits_{\mathbf{K}}j_L(K|\mathbf{r}-\mathbf{r}_i|) \\ \times\rho(\mathbf{K})W_{L\nu i}(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}_i} \\ \times\dfrac{(Q_{L\nu i}-\delta_{L0}Z_i)\delta(|\mathbf{r}-\mathbf{r}_i|)}{4\pi|\mathbf{r}-\mathbf{r}_i|^{L+2}}\Big)W_{L\nu i}(\mathbf{r}-\mathbf{r}_i) \\ 0,\qquad\text{outside }i\text{th sphere} \end{array}\right],$$

$$P_{3L\nu i}(r)=\left[\begin{array}{l} -\delta_{L0}Q_{L\nu i}/\Omega+\dfrac{Q_{L\nu i}\delta(|\mathbf{r}-\mathbf{r}_i|)}{4\pi|\mathbf{r}-\mathbf{r}_i|^{L+2}}W_{L\nu i}(\mathbf{r}-\mathbf{r}_i) \\ -\delta_{L0}Q_{L\nu i}/\Omega,\qquad\text{outside }i\text{th sphere} \end{array}\right],$$

where

$$Q_{L\nu i}=4\pi i^L R_{si}{}^{L+2}\sum_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}_i}j_{L+1}(KR_{si})\rho(\mathbf{K})W_{L\nu i}(\mathbf{K})/K$$
$$-4\pi\int_0^{R_{si}}dr\,r^{L+2}\rho_{L\nu i}(r)+\delta_{L0}Z_i.$$

Each part of the charge denitys is electrically neutral.

The electrostatic potential is a solution of Poisson's equation. The potential $V_{\text{Coul}}(\mathbf{r})$, however, is the potential energy of an electron, and hence is the negative of the electrostatic potential. In the atomic units used, the appropriate Poisson's equation is

$$\nabla^2 V_{\text{Coul}}(\mathbf{r})=8\pi P(\mathbf{r}).$$

By the linearity of this equation, the potential may be expressed as

$$V_{\text{Coul}}(\mathbf{r})=V_1(\mathbf{r})+\sum_{L\nu i}V_{2L\nu i}(\mathbf{r})+\sum_{L\nu i}V_{3L\nu i}(\mathbf{r}),$$

where each part of the potential is due to the corresponding part of the charge density. Historically, the zero of potential has been chosen so that the average value of the potential in the plane-wave region is zero. This convention will be enforced on each of the separate parts of the potential.

*Fourier Series Problem:* $P_1(r)$. The solution to Poisson's equation for $P_1(\mathbf{r})$ can immediately be seen to be

$$V_1(\mathbf{r})=\sum_{\mathbf{K}}G(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}},$$

where

$$G(\mathbf{K})=8\pi\rho(\mathbf{K})/K^2,\quad\text{for }K\neq 0.$$

The arbitrary constant $G(\mathbf{K}=0)$ is chosen so that the average value of the potential outside the sphere is zero.

$$G(\mathbf{K}=0)=-\sum_{\mathbf{K}\neq 0}G(\mathbf{K})\Delta(-\mathbf{K})/\Delta(0)$$

The Fourier series may be reanalyzed to get a new series which gives a step function on the surface of each sphere, and is zero inside each sphere, but which gives the original function in the plane-wave region. Defining

$$G_{L\nu i}(r)=\sum_{\mathbf{K}'}G(\mathbf{K}')i^L W_{L\nu i}(\mathbf{K}')j_L(K'r)e^{i\mathbf{K}'\cdot\mathbf{r}_i},$$

and

$$G_s(\mathbf{K})=\sum_{\mathbf{K}'}G(\mathbf{K}')\Delta(\mathbf{K}-\mathbf{K}'),$$

the desired result is

$$V_1(\mathbf{r})=\left[\begin{array}{l} \sum\limits_{L\nu}G_{L\nu i}(|\mathbf{r}-\mathbf{r}_i|)W_{L\nu i}(\mathbf{r}-\mathbf{r}_i) \\ \sum\limits_{\mathbf{K}}G(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}}=\sum\limits_{\mathbf{K}\neq 0}G_s(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}} \end{array}\right].$$

The series with coefficients $G(\mathbf{K})$ will normally converge rapidly [in the case of an APW charge density, only a small number of charge density coefficients $\rho(\mathbf{K})$ are nonzero, since only a finite number of basis functions are used], while the series with coefficients $G_s(\mathbf{K})$, having a step at the sphere radius, does not converge well. However, for an APW calculation, only the first few coefficients are needed (depending on the number of basis functions used), and these can easily be calculated.

*Zero Multipole Moment Problem:* $P_{2L\nu i}(r)$. The multipole moments $Q_{L\nu i}$ have been defined so that the multipole moment of the charge density $P_{2L\nu i}(\mathbf{r})$ is zero for each sphere. Thus these charge densities give rise to no potential outside the spheres, nor does the charge in one sphere give rise to a potential in any other sphere. The potential inside a sphere is due entirely to the charge density $P_{2L\nu i}(\mathbf{r})$ inside that sphere. Define

$$F_{L\nu i}(r)=\frac{8\pi}{(2L+1)r^{L+1}}\int_0^r dx \times x^{L+2}\left(\rho_{L\nu i}(x)-i^L\sum_{\mathbf{K}} j_L(Kx)\rho(\mathbf{K})W_{L\nu i}(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}_i}\right) +\frac{8\pi r^L}{2L+1}\int_r^{R_{si}} dx \times x^{1-L}\left(\rho_{L\nu i}(x)-i^L\sum_{\mathbf{K}} j_L(Kx)\rho(\mathbf{K})W_{L\nu i}(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}_i}\right).$$

The desired result is then

$$V_{2L\nu i}(\mathbf{r})=\left[\begin{array}{l} -\delta_{L0}\dfrac{2Z_i}{|\mathbf{r}-\mathbf{r}_i|}+\left(F_{L\nu i}(|\mathbf{r}-\mathbf{r}_i|) +\dfrac{2Q_{L\nu i}}{(2L+1)|\mathbf{r}-\mathbf{r}_i|^{L+1}}\right)W_{L\nu i}(\mathbf{r}-\mathbf{r}_i) \\ 0 \end{array}\right].$$

The potential outside the sphere is identically zero, so that no adjustment of the arbitrary constant is needed. The terms involving $Q_{L\nu i}$ will be seen to cancel identical terms in the potential arising from the third part of the charge density, $P_{3L\nu i}(\mathbf{r})$. This is to be expected, since these terms are due to the point multipole moments $Q_{L\nu i}$ which were introduced for convenience in the decomposition of the total charge density. The only true singular contributions to the potential are the nuclear contributions $-2Z_i/r$.

*Generalized Ewald Potential Problem:* $P_{3L\nu i}(\mathbf{r})$. The third and last part of the charge density is an array of point multipole moments of strengths $Q_{L\nu i}$. In the case of $L=0$, the array of point charges (monopoles) is supplemented by a constant charge density to maintain charge neutrality. The potential arising from such an array of multipole moments has been discussed in another paper,[20] where it is shown that the potential is

$$V_{3L\nu i}(\mathbf{r})=\left[\begin{array}{l} -\dfrac{2Q_{L\nu i}\delta_{ii'}W_{L\nu i'}(\mathbf{r}-\mathbf{r}_{i'})}{(2L+1)|\mathbf{r}-\mathbf{r}_i|^{L+1}} \\ -4\pi\delta_{L0}Q_{L\nu i}|\mathbf{r}-\mathbf{r}_{i'}|^2/3\Omega \\ -2Q_{L\nu i}\sum\limits_{L'\nu'} A_{L'\nu'i'}{}^{L\nu i}(2/a)^{L+L'+1} \times|\mathbf{r}-\mathbf{r}_{i'}|^{L'}W_{L'\nu'i'}(\mathbf{r}-\mathbf{r}_{i'}) \\ \sum\limits_{\mathbf{K}} 2Q_{L\nu i}(2/a)^{L+1}U_{\mathbf{K}}{}^{L\nu i}e^{i\mathbf{K}\cdot\mathbf{r}} =\sum\limits_{\mathbf{K}\neq 0} 2Q_{L\nu i}(2/a)^{L+1}U_{s\mathbf{K}}{}^{L\nu i}e^{i\mathbf{K}\cdot\mathbf{r}} \end{array}\right].$$

The generalized Ewald coefficients [20] $A_{L'\nu'i'}{}^{L\nu i}$ and $U_{\mathbf{K}}{}^{L\nu i}$ depend only on the crystal structure, while the step function Ewald coefficients $U_{s\mathbf{K}}{}^{L\nu i}$ depend also on the fraction $R_{si}/R_{si\,\max}$, where $R_{si\,\max}$ is the maximum possible sphere radius for a given structure. The scale is set by the scaling factor $a$, the precise meaning of which is determined by the definition of the dimensionless coefficients $A_{L'\nu'i'}{}^{L\nu i}$ and $U_{\mathbf{K}}{}^{L\nu i}$.

As already mentioned, the singular contributions to $V_{3L\nu i}(\mathbf{r})$, with $r^{L+1}$ in the denominator, are identical, except for sign, to terms in $V_{2L\nu i}(\mathbf{r})$, and so will cancel in the total potential.

## VI. FREE-ELECTRON-EXCHANGE POTENTIAL ENERGY

An approximate expression for the exchange part of the one-electron potential energy is given, assuming that the electronic charge density of the crystal is approximately a muffin-tin charge density, that is, dominantly spherical inside of each APW sphere, and dominantly constant outside the spheres. The average free-electron exchange, given by

$$V_{\mathrm{ex}}(\mathbf{r})=-3(3/\pi)^{1/3}[-P(\mathbf{r})]^{1/3}+C_{\mathrm{ex}},$$

where $C_{\mathrm{ex}}$ is an arbitrary constant, which will be chosen so that the average value of $V_{\mathrm{ex}}(\mathbf{r})$ outside the sphere will be zero, can be expanded using the binomial theorem for the one-third power, and retaining only the first two terms. When this is done, the exchange potential is found to be

$$V_{\mathrm{ex}}(\mathbf{r})=\left[\begin{array}{l} \sum\limits_{L\nu} F_{L\nu i}(|\mathbf{r}-\mathbf{r}_i|)W_{L\nu i}(\mathbf{r}-\mathbf{r}_i) \\ \sum\limits_{K} F_c(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}}=\sum\limits_{\mathbf{K}\neq 0} F_s(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}} \end{array}\right],$$

where

$$F_c(\mathbf{K}\neq 0)=-3(3/\pi)^{1/3}[\rho_{\mathrm{av}}]^{1/3}\rho(\mathbf{K})/3\rho_{\mathrm{av}},$$

$$F_c(\mathbf{K}=0)=3(3/\pi)^{1/3}[\rho_{\mathrm{av}}]^{1/3}\sum_{\mathbf{K}\neq 0}\rho(\mathbf{K})\Delta(-\mathbf{K})/3\rho_{\mathrm{av}}\Delta(0),$$

$$F_{00i}(r)=3(3/\pi)^{1/3}[\rho_{\mathrm{av}}]^{1/3} \times[2\rho_{\mathrm{av}}+\rho(\mathbf{K}=0)+\sum_{\mathbf{K}\neq 0}\rho(\mathbf{K})\Delta(-\mathbf{K})/\Delta(0)]/3\rho_{\mathrm{av}} -3(3/\pi)^{1/3}[\rho_{00i}(r)]^{1/3},$$

and $F_{L\nu i}(r)=-3(3/\pi)^{1/3}[\rho_{00i}(r)]^{1/3}\rho_{L\nu i}(r)/3\rho_{00i}(r)$ for $L\neq 0$.

The series with coefficients $F_c(\mathbf{K})$ converges, while that with coefficients $F_s(\mathbf{K})$ is the step function needed for the APW matrix elements.

## VII. APPLICATION TO LITHIUM

The APW method described in the previous sections has been used to calculate self-consistent energy bands in bcc lithium. The calculations were done on an IBM System/360 Model 65 computer, using programs written

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[20] W. E. Rudge, preceding paper, Phys. Rev. **181**, 1020 (1969); IBM Research Report No. RJ 538 (unpublished).

in the FORTRAN IV language. The monatomic crystal and cubic symmetry lead to a number of simplifications in the formalism. In particular, all the quantities given previously are real. Further, there are nonvanishing cubic harmonics only for $L=0$, 4, 6, 8, $\cdots$, and for $L<12$, there is only one harmonic for each of these $L$'s.

Three separate calculations were done. The first (1) used the exchange potential proposed by Gaspar[16] and by Kohn and Sham[17] and equal to two-thirds of the exchange proposed by Slater.[15] The second calculation (2) used Slater's exchange. Each of these calculations, referred to as full calculations, included non-muffin-tin contributions to the potential and to the charge density. Inside the APW sphere, terms in $L=0$, 4, and 6 were retained, while in the region outside the sphere, the Fourier coefficients for the first 29 inequivalent reciprocal lattice vectors were found and used. For these calculations, energies and charge densities were found in each iteration for the core states at five inequivalent points in the first Brillouin zone, and for the conduction band at 14 inequivalent points. An approximate Fermi surface was found by calculating energies at a total of nine additional points in the $\Delta$, $\Sigma$, and $\Lambda$ directions, and then fitting the function $k(\epsilon,\vartheta,\varphi)$ with quadratics in $\epsilon$ multiplied by the first three cubic harmonics ($L=0$, 4, 6). The Fermi energy $\epsilon_F$ is then simply found by requiring that the surface $k_F=k(\epsilon_F,\vartheta,\varphi)$ enclose the correct volume, namely, one-half of the Brillouin zone. The total charge density was found by summing over states under the Fermi surface.

For comparison, a third calculation (3) was done which used Slater's exchange, but which used only the muffin-tin parts of the potential and charge density. Further, the core states were approximated by an atomiclike $1s$ state, found by a simple radial integration out to the surface of the APW sphere, requiring that the wave function go to zero on that surface. In the conduction band, calculations were done at only five inequivalent points. A spherical Fermi surface was assumed.

In all three calculations, the experimental lattice constant was used as given by Barrett[21]: $a=6.597$ a.u. at 78°K. The APW sphere was taken as large as possible, so that each sphere was tangent to its nearest neighbors.

The vector lists used were sufficiently long to insure convergence in the one-electron energies to better than 0.0003 Ry. The first two calculations were taken through four iterations. The final potentials were within 0.0001 Ry of self-consistency. The third calculation was carried through six iterations, starting with the muffin-tin part of the final charge density from the second calculation. The final muffin-tin potential was within $10^{-8}$ Ry of self-consistency.

TABLE I. One-electron energies from self-consistent APW calculations in lithium for: (1) full calculation using two-thirds of Slater's exchange; (2) full calculation using Slater's exchange; (3) muffin-tin calculation using Slater's exchange. (Energies in rydbergs, wave vectors in units of $2\pi/a$.)

| | | (1) | (2) | (3) |
|---|---|---|---|---|
| Core states | | | | |
| $\Gamma_1$ | (0,0,0) | $-3.016$ | $-3.624$ | |
| $H_1$ | (0,1,0) | $-3.014$ | $-3.623$ | |
| Conduction states | | | | |
| $\Gamma_1$ | (0,0,0) | 0.039 | 0.016 | 0.017 |
| $H_{15}$ | (0,1,0) | 0.680 | 0.665 | 0.670 |
| $P_4$ | $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ | 0.532 | 0.524 | 0.525 |
| $N_1'$ | $(\frac{1}{2},\frac{1}{2},0)$ | 0.309 | 0.302 | 0.303 |
| $\Delta_1$ | $(0,\frac{1}{2},0)$ | 0.210 | 0.194 | 0.195 |
| Excited states | | | | |
| $\Gamma_{15}$ | (0,0,0) | 1.135 | 1.275 | 1.276 |
| $H_1$ | (0,1,0) | 1.244 | 1.177 | 1.177 |
| $H_{12}$ | (0,1,0) | 0.851 | 0.851 | 0.847 |
| $P_1$ | $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ | 0.881 | 0.831 | 0.836 |
| $N_1$ | $(\frac{1}{2},\frac{1}{2},0)$ | 0.522 | 0.497 | 0.499 |
| $N_3'$ | $(\frac{1}{2},\frac{1}{2},0)$ | 1.018 | 0.994 | 0.998 |
| $N_4'$ | $(\frac{1}{2},\frac{1}{2},0)$ | 1.127 | 1.105 | 1.103 |
| $\Delta_1$ | $(0,\frac{1}{2},0)$ | 1.186 | 1.144 | 1.143 |
| $\Delta_5$ | $(0,\frac{1}{2},0)$ | 0.893 | 0.876 | 0.880 |
| Fermi energy $\epsilon_F$ | | 0.289 | 0.278 | |
| Asphericity | | 2.87% | 2.32% | |

The self-consistent energies from a few points of high symmetry are shown in Table I. Also given are the Fermi energy and the asphericity of the Fermi surface, defined as the per cent of the average radius equal to the maximum deviation. The energy bands for the full calculation (2) using Slater's exchange are shown in Fig. 1. Note that while the conduction bands are accurately plotted, the excited bands were calculated only at a relatively few points of high symmetry. The bands for the other two calculations do not differ significantly from those shown in Fig. 1, and hence were not plotted.

As is well known, the potential and charge density in lithium are both very nearly muffin tin in form, and this is reflected in the closeness of the results of calculations (2) and (3). The greater difference is between (1) and (2), showing that in lithium, at least, the choice of exchange potential is of greater importance than whether or not the non-muffin-tin contributions are included in the calculation.

Following Ham,[22] the energy bands near $\Gamma_1$ can be fit in the spherical form

$$\epsilon(k)=\epsilon_0+\epsilon_2k^2+\epsilon_4k^4,$$

where the coefficients $\epsilon_0$, $\epsilon_2$, and $\epsilon_4$ are chosen by a least-squares fit to 13 calculated points at $\Gamma$ and along $\Delta$ and $\Lambda$ up to the Fermi surface, but along $\Sigma$ only half way to $N$, thus avoiding the distortion in the bands in this direction. Further, to describe the bulge, Ham uses the following form for the energy along the $\Sigma$ direction near $N$, derived from a nearly-free-electron model:

$$f(u)=\epsilon(N_1')+V_1+\xi u^2-(\omega u^2+V_1^2)^{1/2},$$

where $u$ is the distance from $N$, along $\Sigma$; $\epsilon(N_1')$ is the energy of $N_1'$; and $V_1$ is half of the (positive) energy gap

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[21] C. S. Barrett, Acta Cryst. **9**, 671 (1956).

[22] F. S. Ham, Phys. Rev. **128**, 82 (1962); **128**, 2524 (1962).

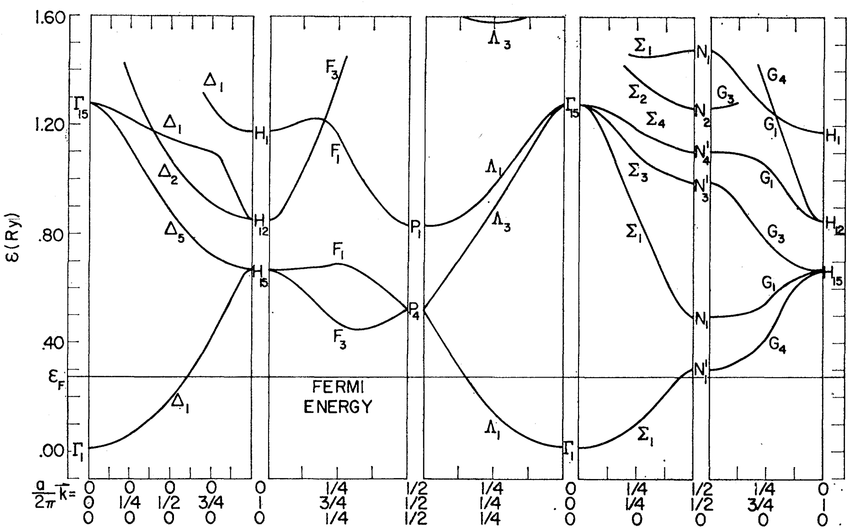

FIG. 1. Self-consistent energy bands for bcc lithium, found by full APW calculation (2) using Slater's exchange. Lattice constant $a=6.597$ a.u.

at $N$. The parameters $\xi$ and $\omega$ are chosen so that $f(u)$ gives the calculated energies at $\Sigma_1(\frac{1}{4},\frac{1}{4},0)$ and $\Sigma_1(\frac{3}{8},\frac{3}{8},0)$.

The various parameters have been fit to the results of the two full APW calculations (1) and (2), and are given in Table II along with the results of Ham interpolated to the same lattice constant. $\epsilon_0$ has not been given, since it depends on the arbitrary choice of zero energy.

Using the fitting scheme described, Ham also finds the density of states $n(\epsilon)$ and hence the Fermi energy $\epsilon_F$ by requiring that

$$\int_{\epsilon_0}^{\epsilon_F} d\epsilon n(\epsilon) = \Omega^{-1}.$$

TABLE II. Comparison of quantities for lithium found from APW calculations (1) and (2) with those of Ham,[a] interpolated to the same lattice constant $a=6.597$ a.u.

| | APW(1) | APW(2) | Ham |
|---|---|---|---|
| $\epsilon_2$ | 0.7468 | 0.7825 | 0.752 |
| $\epsilon_4$ | 0.0084 | −0.0116 | 0.004 |
| $\xi$ | 0.7872 | 0.7862 | 0.7681 |
| $\omega$ | 1.1337 | 1.1677 | 1.1133 |
| $V_1$ | 0.1064 | 0.0976 | 0.1045 |
| Thermal effective mass $m_t/m_0$ | 1.6510 | 1.5477 | 1.66 |

[a] Reference 22.

The thermal effective mass $m_t/m_0$ may be expressed in terms of the density of states at the Fermi surface.

Using Ham's method, the Fermi energies for the two APW calculations were found to be only about 0.002 Ry lower than when calculated by the method described earlier. The thermal effective masses found are given in Table II, along with the results of Ham.

It is interesting to note that Ham's results, the product of a Green's-function calculation and the quantum defect method, generally lie between the two APW results, and a little closer to APW(1), which used two thirds of Slaters exchange potential.

## VIII. CONCLUSIONS

The APW method is not limited to the traditional muffin-tin form, and expressions for the more general form have been given. The feasibility of carrying out such a calculation on a modern computer has been shown by an application to lithium.

## ACKNOWLEDGMENTS

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